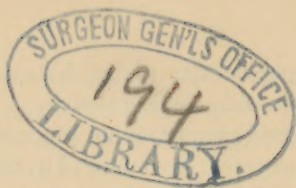


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[From AMERICAN CHEMICAL JOURNAL, Vol. III, No. 3, June, 1881.]

ON THE MOLECULAR WEIGHT OF HYDROFLUORIC ACID.¹

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The analogies of fluorine with the halogens on the one hand and with oxygen on the other have often been remarked upon. The general resemblance of fluorine compounds to the corresponding compounds of chlorine is manifest, and the two elements are usually classed together; but some striking differences force themselves upon the attention, such as those existing between the chloride and fluoride of calcium, chloride and fluoride of silver, etc., and the marked tendency of the fluorides to the formation of double salts with formulæ analogous to those of oxygen compounds, as well as the formation of many salts including both oxygen and fluorine, suggests some close natural relation between these elements themselves.

When the principle of quantivalence or atomicity first began to assume distinct shape, it became a matter of special interest to decide whether fluorine should be classed with chlorine amongst the monad elements, with the formula HF for hydrofluoric acid, and the atomic weight 19 for fluorine itself, or should be placed with oxygen amongst the dyads, writing H₂F for hydrofluoric acid, and assuming the atomic weight of fluorine as 38. For some time, although analogies were chiefly in favor of the former view, no direct evidence was available for the settlement of this question, but in 1869 it seemed to be supplied by the researches of Gore,² who, heating silver fluoride in contact with an equivalent quantity of pure and dry hydrogen, observed that "one volume of hydrogen in uniting with fluorine produces, not simply one volume of gaseous product, as it does when uniting with oxygen, but two volumes, as in the case of its union with chlorine." Further on, in the same

¹The substance of this paper was verbally presented, by invitation, at the meeting of the National Academy of Sciences at Washington, April 22, 1881.

²Philosophical Transactions for 1869. A further paper, on silver fluoride, appeared in 1870.

paper, after giving his results as to the amount of silver in the fluoride used, he says: "These results, combined with the foregoing experiments on molecular volume, agree with the conclusion that a volume of hydrogen weighing 1 unites with 19 parts by weight of fluorine to form 2 volumes of hydrofluoric acid, and that the specific gravity of gaseous anhydrous hydrofluoric acid is ten times the amount of that of hydrogen."

Gore's experiments were made with somewhat small quantities of the materials used (about a gram of silver fluoride and 90 or 100 cubic centimetres of hydrogen), and in opaque vessels of platinum, the volume assumed by the gaseous hydrofluoric acid being ingeniously determined by raising or lowering the cylindrical platinum receiver, so that the level of the mercury in which it was placed remained the same inside and out, and reading off an external scale. The whole apparatus was heated in an air-bath to 93° – 100° C. before making the final reading. It is stated that fourteen separate attempts were made to ascertain the volume of gaseous product formed, but the numerical results of only two of these are given. They seem fairly to establish the fact that at temperatures near 100° hydrofluoric acid exists as HF, 93.3 and 98.5 per cent. respectively of the theoretical volume being obtained after allowance for expansion at the temperature employed. The atomic weight of fluorine is thus established as 19, not 38.

Certain measurements of the gaseous acid are, however, given for lower temperatures, though far above the boiling point (67° F., as found by Gore himself= 19.5° C.) which represent distinctly smaller volumes. Thus at 139° F. (59.5° C.) the volume was but 85.8 per cent. of that required by theory, and at 160° F. (71° C.) it was 88.1 per cent.

Hence it seemed still desirable to try to ascertain whether the acid exhibits a different but definite vapor density at a temperature nearer the boiling point, though high enough to preclude any actual liquid acid remaining, operating on quantities large enough to give decisive results with even rough weighings, and if possible in transparent or translucent vessels. With this object in view I have made the following experiments.

Perfectly pure Greenland cryolite, carefully selected in choice fragments, was pulverized in a clean iron mortar, heated to 300° C. for some time, and transferred while still warm to a well dried and warm bottle. Sulphuric acid was prepared of full strength by

adding to a quantity of the purified acid of 95 or 96 per cent. a small excess of pure sulphur trioxide, and passing for several hours a well dried and gently warmed current of air through the liquid ; this was also preserved in a well stoppered bottle until needed. The cryolite and acid were heated together in a leaden retort, the capital of which was clamped on without lute, and the hydrofluoric acid vapor given off was conducted downwards through a worm of leaden tube, 6 mm. in interior diameter and 3.5 metres long, surrounded by crushed ice, into a leaden bottle cooled by a freezing mixture of ice and salt. The interior of all the leaden apparatus had been previously crusted over by passing hydrofluoric acid vapor through for some time. The joints were made by simply wrapping tightly with lead foil, and ligating with wire. The quantity of the materials used was such as to produce eight times the amount of hydrofluoric acid necessary to fill with vapor the leaden bottle and the flask and connecting tubes to be afterwards used, even assuming the highest vapor density that could well be expected.

The flask in which the vapor was to be weighed was of good Bohemian glass, and held nearly $4\frac{1}{2}$ litres, being as large as could be well managed in the balance case. It was slung in a light network of platinum wire, with a suspending ring at top, and was, after thorough drying, carefully coated over the whole inside surface with clear, colorless paraffine,¹ poured in in the melted state, and evenly distributed by turning round and round the gently-warmed flask. The melting point of the paraffine was 56° C., well above the temperature to be afterwards applied. The neck of the flask was accurately fitted with a sound, soft cork, previously well dried and soaked in paraffine. Through this cork passed two glass tubes of about 5 mm. bore, one of which extended about two-thirds of the way to the bottom of the flask, and just above the cork was bent at right angles, the short projecting limb being some 20 mm. long. The other tube ended just below the cork on the inside of the flask, came out straight, and projected also about 20 mm. on the outside. Both were drawn down a little in diameter, about 5 mm. from the outside ends, so as to form a little socket for the small cork by which each tube was to be closed, insuring this cork

¹The dry acid in the gaseous state does not act upon glass, but, as it did not seem certain that, by the process used, perfect exclusion of moisture would be secured, it was thought better to take this precaution

coming to exactly the same position when inserted. The two small corks, the whole of the interior of the glass tubes, and so much of their exterior surface as was to be inside the flask were thoroughly protected by paraffine. The specific gravities of the glass, paraffine, platinum and paraffine-coated corks with tubes were taken at about the temperature to be used, and the figures obtained corrected for buoyancy in air by the formula—

$$G_r = G_a - \rho(G_a - 1)^1$$

From the thus corrected specific gravities, and careful weighings in air of observed temperature and pressure, the volumes and absolute weights *in vacuo* of all the materials concerned were deduced, save in the case of the hydrofluoric acid vapor itself, the volume of which was obtained by an actual calibration² of the part of the flask and tubes occupied by it.

As soon as the distillation of the acid and its collection in the leaden bottle was complete, the retort and capital were disconnected from the worm, and the upper end of the latter connected with the bent tube of the paraffine-lined flask, interposing in the first experiment another small flask, also protected by paraffine, and containing a little phosphorus pentoxide, as the means of removing any last traces of aqueous vapor. Removing the freezing mixture from about the leaden bottle, the latter was surrounded with water at 25° C., and the water surrounding the worm was brought to the same temperature, while the flask was at 1° or 2° lower. The hydrofluoric acid thus vaporized filled the whole apparatus, gradually expelling the air, and the excess escaped through a long India-rubber tube attached to the exit glass tube, and carried through a hole in the door-casing to the outside atmosphere, thus avoiding danger to the lungs and eyes, and risk of corrosion of the outside of the flask. When the escape of vapor slackened, the two tubes entering the flask were quickly disconnected from the rest of the apparatus and the little paraffine-soaked corks at once inserted. In doing this but one tube at a time was open, and that but for a moment.

¹ G_r being the real specific gravity of the body, G_a the apparent specific gravity of same taken without air correction by simple weighings in air and water, and ρ the ratio of the densities of air and water under existing conditions of temperature and pressure.

²With water of known temperature, as the weight of mercury necessary would hardly have been safely borne by the flask.

The flask was then placed in a deep cylinder of sheet zinc, of diameter to just fit it, and this was immersed in a much larger cylinder, containing some 30 litres of water, at a little over 30° C., a cover with small openings in it being fitted over both. Previous experiment with a similar flask of air and enclosed thermometer showed what small allowance to make in the temperature of the water in order to bring the flask and its gaseous contents to the desired point. In the actual experiments with hydrofluoric acid a thermometer was placed on the upper part of the outside of the flask, while another was immersed in the water of the outer vessel. From time to time, as the temperature of the flask rose, the little cork was partly withdrawn for a moment from the straight vertical exit tube, and the surplus vapor was thus allowed to escape. In doing this one or two small, but bad, burns were made upon the fingers by the frightfully corrosive dry acid, of whose dangerous character one can hardly speak too strongly.

When the temperature of the flask had become stationary at or very close to 30° the little corks were firmly inserted in their seats, the flask was removed from the zinc cylinder, allowed to cool to the temperature of the balance-room, which had, however, been warmed up for several hours by a stove to a little over 25° , and was then accurately weighed.

The following result was obtained in the first experiment :

Weight of flask, etc., and vapor, *in vacuo*, 393.781 grams.

“ “ empty, “ 386.531 “

Weight, *in vacuo*, of 4347.4 cc. of vapor

at 29° C. and 743.7 mm. (cor.) =

3846 cc. at 0° C. and 760 mm., 7.250 grams.

Hence, 1 liter of vapor at 0° and 760 mm. = 1.885 grams.

Hence, sp. gr. of vapor ($H^* = 1$) = 21.06,

or molecular weight = 42.12.

As soon as the weighing was over the flask was washed out with distilled water enough to largely dilute the acid, into a platinum dish, and the purity of the liquid examined. It was quite clear and free from silicon or lead, and gave no reaction for sulphuric or sulphurous acid, but on testing with ammonium molybdate very distinct evidence was obtained of the presence of phosphoric acid.

*One liter of hydrogen at 0° and 760 mm. at Univ. of Va. = .089488 gram.

This had been suspected from the energy with which the phosphorus pentoxide, of which fortunately but little had been used, was attacked by the vapor. In all probability phosphorus pentafluoride had been formed and carried forward with the hydrofluoric acid. This may serve to account for the vapor density of the latter coming out somewhat too high for even the formula H_2F_2 (requiring sp. gr. = 20). Any traces of air or aqueous vapor which might have been present would, of course, have tended on the contrary to produce a lower result.

In order to avoid this ascertained source of error in a second experiment, the phosphorus pentoxide was omitted altogether, the upper end of the leaden worm was directly connected to the large flask, and as the means of finally drying the vapor, a little sulphuric acid of full strength (pure H_2SO_4 —not SO_3) was added to the liquid hydrofluoric acid in the leaden bottle while it was still in the freezing mixture, before proceeding to vaporize the latter acid at the very moderate temperature of 25° . A new flask, lined with paraffine and fitted with tubes as before, was used, and the following result was obtained:

Weight of flask, etc., and vapor <i>in vacuo</i> ,	428.255 grams.
“ “ empty “	421.436 “

Weight, *in vacuo*, of 4394.7 cc. of vapor
 at 30.5° C. and 745.2 mm. (cor.) =
 3876.5 cc. at 0° C. and 760 mm., 6.819 grams.
 Hence, 1 litre of vapor at 0° and 760 mm. = 1.759 gram.
 Hence, sp. gr. of vapor ($H = 1$) = 19.66,
 or molecular weight = 39.32.

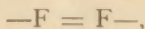
In this case the dilute acid washed out from the flask after the experiment seemed to be quite pure, or at any rate was free from silicon, lead, sulphuric and sulphurous acids. In both experiments the flask was, immediately after weighing, carefully inspected in a strong light, and no visible trace of liquid could be observed on the inside surface.

The glass, examined after removal of the paraffine, was found quite uninjured, except a slight trace of corrosion on the outside close to the exit.

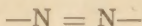
The figures obtained obviously justify the assumption that at 30° C. the molecule of hydrofluoric acid vapor should be repre-

sented not as HF, but as H_2F_2 , since the agreement with this assumption of the vapor density obtained in the two experiments is too close to be fairly accounted for by the mere general idea of imperfect gaseous condition, and it is certain that no such quantity of actually liquid acid as would be necessary to account for the double weight could possibly have escaped detection on the inner surface of the flask. At higher temperatures, such as those at which Gore's measurements were made, dissociation manifestly takes place, leading to the production of diatomic molecules of HF.

The structure of the molecule of double weight, H_2F_2 , may be well viewed as resulting from fluorine behaving not only as a monad but also as a triad, and acting in double atoms,



like those of nitrogen,



in the di-azo compounds. In such a condition the element presents a pseudo-dyad character, and becomes capable of replacing oxygen, and manifesting the *linking* function of the latter. Admitting, therefore, that the atomic weight of fluorine remains fixed at 19, we can see that the molecule of hydrofluoric acid may at high temperatures be $H-F$, analogous to that of hydrochloric acid, while at a little above the boiling point under ordinary pressure the structure may be $H-F=F-H$, and thus analogous to that of water.¹

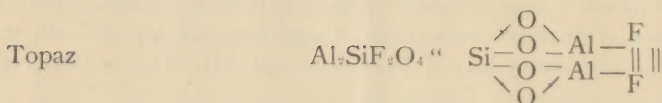
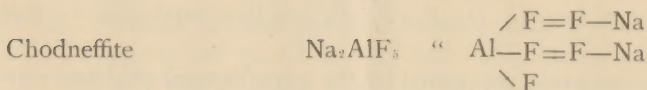
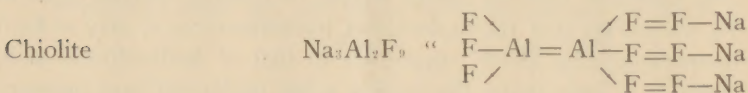
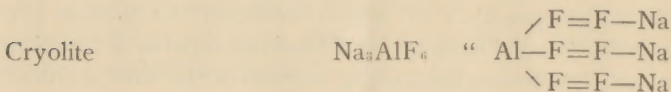
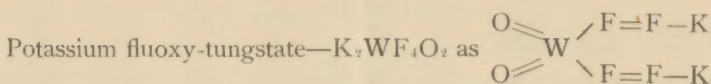
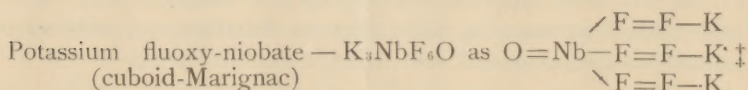
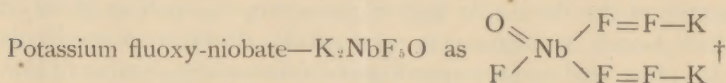
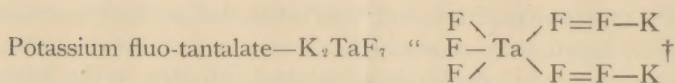
This assumption, supported by the experimental evidence now brought forward, serves conveniently to explain the constitution of a number of fluorine compounds, whose formulæ are difficult to write in a satisfactory way if fluorine be considered as exclusively monad.

Thus we may view :

Potassium hydro-fluoride— KHF_2 as $K-F=F-K$

Potassium boro-fluoride— KBF_4 “ $\begin{array}{c} F \\ || \\ F \end{array} \diagup \diagdown B-F=F-K$

¹ Gore sums up the results of his numerous experiments on the chemical behavior of this interesting substance with the sentence: “From the various experiments already described, we may conclude that hydrofluoric acid is by its properties placed between hydrochloric acid and water, but is much more closely allied to the former than to the latter.”

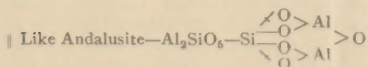


* On the type of a meta-silicate. Like formulæ apply to the analogous compounds of titanium, zirconium and tin.

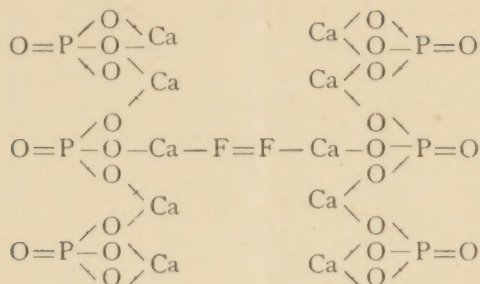
† Or these formulæ may be doubled, so as to correspond exactly with the oxygen pyro-tantalate and pyro-niobate.

‡ On the type of an ortho-niobate.

§ As for the normal tungstate. The case of the fluoxy-molybdate is of course the same.



Apatite— $\text{Ca}_5\text{P}_3\text{FO}_{12}$ —might be written :



but, in view of the replacement of fluorine by chlorine in this mineral, as in the analogous pyromorphite and mimetite, it is doubtless better, as well as simpler, to suppose the molecule to be merely—

